THREE-D GEOCONSULTANTS LIMITED

Open File Report 90-16

COMPARATIVE QUANTIFICATION OF PYRIDINE-TYPE COMPOUNDS IN NEW BRUNSWICK AND COLORADO SHALE OILS

by

THREE-D GEOCONSULTANTS LIMITED

Canada-New Brunswick Mineral Development Agreement

Entente Canada-Nouveau-Brunswick L'Exploitation Minérale

Natural Resources and Energy New Brunswick

Ressources Naturelles et Énergie Nouveau-Brunswick

Energy, Mines and Resources Canada

Énergie, Mines et Ressources Canada

Price $2.00

This report has been prepared for:

Energy Branch
Department of Natural Resources and Energy
Province of New Brunswick

Hon. Morris Green, Minister

December, 1990

This report should be referenced in the following manner:

THREE-D GEOCONSULTANTS LIMITED. 1990. Comparative quantification of pyridine-type compounds in New Brunswick and Colorado shale oils. New Brunswick Department of Natural Resources and Energy, Mineral Resources, Open File Report 90-16, 27 p.

91-02738/

COMPARATIVE QUANTIFICATION OF PYRIDINE-TYPE COMPOUNDS IN NEW BRUNSWICK AND COLORADO SHALE OILS

This project was funded under the Canada-New Brunswick Mineral Development Agreement, a subsidiary agreement under the Economic and Regional Development Agreement.

Copies available by contacting:

Mineral Resources
Department of Natural Resources and Energy
P.O. Box 6000, Fredericton
New Brunswick E3B 5H1

December, 1990

Report No.: Open File Report 90-16

Author: Three-D GeoConsultants Limited

Catalogue No.: ISSN 0712-4562

THREE-D GEOCONSULTANTS LIMITED

P.O. Box 3133, Station B, Fredericton, N.B. E3A 5G9
Suite B4, 108 Prospect Street West
Tel: (506) 453-7700 Fax: (506) 453-9861

1990 10 15

New Brunswick Department of
Natural Resources and Energy
Energy Branch
P.O. Box 6000
Fredericton, N.B.
E3B 5H1

Attention: C. St. Peter

Dear Mr. St. Peter

Re: COMPARATIVE QUANTIFICATION OF PYRIDINE-TYPE COMPOUNDS IN NEW BRUNSWICK AND COLORADO SHALE OILS

I am pleased to submit the final edition of this report for your perusal.

It might be of interest to note that at last June's meeting of the Minister's National Advisory Council to CANMET it was apparent that there is considerable interest in asphalt quality. The possibility of dumping nitrogen, stripped from crude oil, into asphalt is of particular interest. CANMET researchers and industry officials alike appreciate the utility of pursuing all avenues of research directed at asphalt quality.

Yours truly

THREE-D GEOCONSULTANTS LTD.

F.D. Ball
Senior Geologist

EXECUTIVE SUMMARY

In the United States, sectors of the oil shale industry have recognized the market potential for shale oil in asphalt production. Studies involving Green River Formation shale oil have suggested that shale-oil-based asphalt enhance pavement durability. The evidence indicates that basic, probably pyridinic, nitrogen compounds are responsible for the observed increased moisture resistance of shale-oil-derived asphaltic concretes. Blends consisting of petroleum asphalt and up to 20% shale oil asphalt exhibit balanced characteristics of improved resistance to both moisture damage and oxidative hardening. In addition, it was found that nitrogen-bearing additives derived from both shale oil and from coal liquids enhance pavement flexibility and durability upon recycling.

This study had as its objective the comparative analyses of New Brunswick shale oil relative to Green River shale oil in order to determine the potential of the former as feedstock for the production of asphalt exhibiting enhanced durability. A suitable extraction procedure for isolating the basic nitrogen component found in shale oils was developed. Elemental, infrared and gas chromatographic analyses were then used to quantify the concentration of basic elemental nitrogen in the basic nitrogen extracts. The concentration of basic elemental nitrogen in the raw shale oils was then calculated.

The concentration of basic elemental nitrogen in raw New Brunswick shale oil, at 0.11 to 0.14 wt.%, is 32 to 41% of that in Colorado shale oil (0.34 wt.%). However, the question of whether the properties of enhanced pavement durability observed in shale-oil-based asphalt are directly proportional and solely attributable to their content of basic nitrogen components remains unresolved. Shale oil asphalt production, blending and performance testing is the only method of true evaluation of performance. In order to unequivocally determine whether New Brunswick shale oils offer any potential as a source of asphalt having superior durability, it will be necessary to produce samples of shale oil asphalt for

testing purposes. These asphalt must then be characterized and used in the preparation of samples of asphaltic concretes and tested in a manner similar to those procedures used in testing conventional asphaltic concretes.

RÉSUMÉ EXÉCUTIF

Aux Etats-Unis, le secteur de l'industrie des schistes bitumineux a reconnu le potentiel du marché des huiles de schistes dans la production d'asphalte. Des études portant sur l'huile de schiste de la formation de Green River suggèrent une durabilité accrue du pavé fait à partir d'huile de schiste. Les résultats indique que des composés basique d'azote, probablement pyridinique, sont responsables pour la plus grande résistance à l'humidité des bétons asphaltés faits à partir d'huile de schiste. Des mélanges consistant d'asphalte à base de pétrole et jusqu'à 20% d'asphalte à base de schiste démontrent des caractéristiques balancées d'amélioration de résistance aux dommages causés par l'humidités etau durcissement oxydatif. De plus, les additifs azotés provenant del'huile de schiste et des liquides de charbon accroisseraient la flexibilité et la durabilité du pavé une fois celui-ci recyclé.

Cette étude avait pour but l'analyse comparative entre l'huile de schiste du Nouveau-Brunswick et celle de Green River afin de déterminer le potentiel de cette première comme source d'approvisionnement pour la prodution d'asphalte de plus grande durabilité. Une méthode d'extraction pour isoler le composant basique d'azote trouvé dans l'huile de schiste fût développée. Des analyses élémentaires, à l'infra-rouge, et au gaz chromatographique furent par la suite utilisées pour déterminer la concentration de l'azote élémentaire basique dans les extraits basique d'azote. La concentration de l'azote élémentaire basique dans l'huile de schiste brute fût alors calculée.

La concentration de l'azote élémentaire basique dans l'huile de schiste du Nouveau-Brunswick, de 0.11% à 0.14% du poid, est de 32 à 41% de celle de l'huile de schiste du Colorado (0.34% du poid). Cependant, la question voulant que les propriétés de durabilité accrue de l'asphalte observées dans l'asphalte à base d'huile de schiste soient directement proportionnelles et uniquement attribuable à leur teneur en composants basique d'azote demeure non-résolue. La production d'asphalte d'huile de schiste, le melange et l'épreuve de performance demeurent toujours la seule

méthode d'évaluation réelle de performance. Afin de pouvoir déterminer sans équivoque si les huiles de schistes du Nouveau-Brunswick offrent quelque potentiel comme source d'asphalteà durabilité supérieure, il sera nécessaire de produire des échantillons d'asphalte d'huile de schiste pour fin d'analyse. Ces asphaltes devront par la suite être caractérisés et utilisés dans la préparation d'échantillons de béton asphalté, et mis à l'épreuve d'une manière semblabe aux méthodes utilisées pour épreuves des bétons asphaltés conventionnels.

TABLE OF CONTENTS

Letter of transmittal

Executive summary i

Résumé exécutif iii

Table of contents v
List of tables v
List of appendices v

1.0 Introduction 1
1.1 Background 1
1.2 Objective 2
1.3 Scope 3

2.0 Analytical procedures 4
2.1 Acquisition of samples 4
2.2 Development of analytical technique 4
2.3 Analyses 5

3.0 Results 7
3.1 Raw shale oil 7
3.2 Shale oil extracts 7

4.0 Conclusions 11

5.0 Recommendations 13

6.0 References 17

LIST OF TABLES

Table 1 Nitrogen analyses results 8

LIST OF APPENDICES

Appendix 1 Infrared spectrum of the raw shale oils 18

1A Infrared spectrum of the raw Colorado shale oil 19

1B Infrared spectrum of the raw Albert Mines (New Brunswick) shale oil 20

	1C	Infrared spectrum of the raw Dolomite Marlstone (New Brunswick) shale oil	21
Appendix	2	Infrared spectrum of the extracted basic nitrogen fractions	22
	2A	Infrared spectrum of the basic nitrogen fraction extracted from the Colorado shale oil	23
	2B	Infrared spectrum of the basic nitrogen fraction extracted from the Albert Mines (New Brunswick) shale oil	24
Appendix	3	Gas chromatograph traces of the extracted basic nitrogen fractions	25
	3A	Gas chromatograph trace of the basic nitrogen fraction extracted from the Colorado shale oil	26
	3B	Gas chromatograph trace of the basic nitrogen fraction extracted from the Albert Mines (New Brunswick) shale oil	27

1.0 INTRODUCTION

1.1 BACKGROUND

There is a recent trend in oil refining to process the residual or heavy bottom end of the crude oil barrel into lighter distillates and transportation fuels, at the expense of producing petroleum binders for asphalt. In addition, given the fluctuations in world crude oil markets of the past decade and a half, sources of refinery feedstock are not necessarily fixed with the result that crude oil characteristics and resultant asphalt properties vary. These factors have been identified as major contributors to an increasing number of road pavement problems. The problems are exacerbated by the significant increase in traffic volume and increased truck weights in recent years and the advanced age of the North American highway system.

In the United States, sectors of the oil shale industry have recognized the market potential for shale oils in asphalt production. Interested parties in New Brunswick, where reserves of oil shale have been identified, have seen potential in the utilization of shale oil in the production of asphalt. The Energy Branch of the New Brunswick Department of Natural Resources and Energy commissioned a study to evaluate New Brunswick shale oil for its potential as an asphalt feedstock (Three-D GeoConsultants Ltd., 1989). The report details research which suggests that shale-oil-based asphalt enhance pavement durability. The evidence indicates that basic, probably pyridinic, nitrogen compounds are responsible for the observed increased moisture resistance of shale-oil-derived asphaltic concretes. Blends consisting of petroleum asphalt and up to 20% shale oil asphalt exhibit balanced characteristics of improved resistance to both moisture damage and oxidative hardening. In addition, it was found that nitrogen-bearing additives derived from both shale oil and from coal liquids enhance pavement flexibility and durability upon recycling.

Shale oils derived from the Albert Formation in New

Brunswick are nitrogen-bearing but no information exists to indicate the type or quantity of the various nitrogen compounds known to be present. It has been determined that the use of New Brunswick shale oil as a feedstock for the production of asphalt to be blended with conventional petroleum asphalt or for the production of asphalt recycling agents is worthy of further consideration. It was recommended that a suitably sized sample of New Brunswick shale oil be acquired, analyzed and distilled to yield a sample of asphalt. The shale oil asphalt could then be blended and the appropriate tests conducted to determine whether New Brunswick shale oil asphalt possess enhanced durability characteristics.

This report presents the findings of a study which undertook the initial portion of the recommended work, that is the acquisition of samples of New Brunswick and Green River Formation (specifically from the State of Colorado) shale oil and the analysis of those samples. The Green River shale oil is the basis for the relevant shale oil asphalt studies completed in the United States. Comparative analytical data constitutes the first step in evaluating the potential of New Brunswick shale oil as an asphalt feedstock. The necessity of having to produce a sufficient quantity of New Brunswick shale oil was not a prerequisite to the proposed study. The shale oil retorted from the New Brunswick oil shale samples shipped to Petroleo Brasileiro by Canadian Occidental Petroleum Ltd. in October, 1988 (Filho et al., 1989) was available for the purpose of this study.

1.2 OBJECTIVE

The objective of the study was to analyze and compare New Brunswick shale oil and Green River shale oil in order to determine the potential of the former as feedstock for the production of asphalt exhibiting enhanced durability.

1.3 SCOPE

The objective of the study was met through the successful development and application of a suitable extraction procedure for isolating the basic nitrogen compounds found in the shale oil samples from both New Brunswick and Colorado. Elemental and infrared analyses were then used to quantify the concentration of basic elemental nitrogen in the basic nitrogen extracts. Gas chromatographs of the basic nitrogen extracts were completed to supplement the analytical data. Development and application of the extraction procedure and the analyses were completed by the Process Chemistry Department of the New Brunswick Research and Productivity Council.

2.0 ANALYTICAL PROCEDURES

2.1 ACQUISITION OF SAMPLES

A 3.8 litre sample of Green River Formation shale oil was acquired from Mr. L. Lukens of the New Paraho Corporation, Colorado. New Paraho is involved in the production and testing of shale oil and shale oil asphalt in the United States.

Two 1.0 litre samples of Albert Formation shale oil were acquired from the stock of shale oil returned to the New Brunswick Department of Natural Resources and Energy by Petroleo Brasileiro S.A. The stock resulted from retorting tests completed using the Petrobras Petrosix Process (Filho et al., 1989). Petrobras had retorted two samples of oil shale taken from the Albert Mines Deposit in New Brunswick; one from the Albert Mines zone and one from the dolomite marlstone zone. Petrobras designated the resultant shale oils as Run 213 and 212, respectively. The shale oil samples returned by Petrobras are stored in separate 76 litre plastic carboys in the drill core storage facility of DNRE in Fredericton. The carboys were held at room temperature for 24 hours and the contents of each very thoroughly mixed prior to extracting the representative 1.0 litre samples which were to be used in this study.

2.2 DEVELOPMENT OF ANALYTICAL TECHNIQUE

Previous workers (Plancher and Petersen, 1984) provide an outline of the technique employed to determine the concentration of basic aromatic nitrogen compounds in shale oils. The technique involves concentrating the nitrogen compounds found in a sample of shale oil then performing an infrared analysis on the sample. Although the techniques employed are standard, their use with shale oils is not, therefore this study purposely incorporated a program of technique development and testing. This program was designed to

assure the production of quantifiable and reproducible results.

The three samples of shale oil, one from Colorado and two from New Brunswick were, upon receipt by the Research and Productivity Council, subject to:

1) infrared spectrum analyses (Nicolet FTIR), the results of which are presented in Appendix 1.
2) analyses of total elemental nitrogen content (LECO), the results of which are present on Table 1.

Plancher and Petersen (1984) utilized a technique which involved the extraction of a basic nitrogen fraction through the reaction of HCl gas with the shale oil at a temperature of 43°C and a pressure of 55.2 kPa. The procedure resulted in the precipitation of hydrochloride salts of the nitrogen compounds. Application of this technique yielded 1.3 wt% basic nitrogen fraction in Colorado shale oil. Researchers at the Research and Productivity Council, however, were not clear how this fraction was then isolated from the shale oil. Due to this uncertainty a procedure was developed to extract the basic nitrogen fraction from the shale oil.

2.3 ANALYSES

The procedure developed was performed in duplicate on each of the three shale oil samples. A 20 g liquot of shale oil was dissolved in 150 ml of petroleum ether and extracted three times with 150 ml of 0.6M HCl. The combined aqueous extracts, containing the basic nitrogen components in the form of their hydrochloride salts, were neutralized with 6M NaOH to liberate the basic nitrogen component from the salt form. The aqueous phase was extracted three times with 100 ml methylene chloride. The combined methylene chloride extracts were dried with magnesium sulphate and evaporated at room temperature to remove only the methylene chloride. The basic nitrogen fraction was then weighed and its IR spectrum and

total elemental nitrogen content measured. Infrared analysis of the extracts also confirmed any interferences from the solvents used in the procedure.

Gas chromatographic analyses of the basic nitrogen extracts were completed in an effort to provide additional background analytical data. These analyses consisted of dissolving the samples in methylene chloride and injection onto a 30 mm Durawax capillary column. The instrument used was a Perkin Elmer gas chromatograph equipped with a flame ionization detector.

3.0 RESULTS

3.1 RAW SHALE OIL

The raw Colorado shale oil contains 1.92% elemental nitrogen whereas the Albert Mines and dolomite marlstone shale oils contain 1.07% and 0.97% elemental nitrogen, respectively (Table 1). The New Brunswick shale oils therefore contain between 50.5% and 55.7% of the elemental nitrogen contained in the Colorado shale oil. These values correspond to those published previously by other workers (St. Peter, 1984). This correspondence indicates that in terms of total elemental nitrogen content, the samples acquired for this study were reasonably representative of the shale oils retorted by various other workers from both the New Brunswick and Colorado oil shales.

The infrared spectra of the three raw shale oils (Appendix 1) show no major differences. The medium absorption bands in the 1600 to 1635 cm^{-1} region of the spectra of all three shale oils indicate the presence of aromatic components.

3.2 SHALE OIL EXTRACTS

The elemental nitrogen analyses of the basic nitrogen extracts (Table 1) show the expected increase in the nitrogen component. The extraction procedure developed for this study results in more than a 4-fold increase in the wt.% of the basic nitrogen fraction over the method reported by Plancher and Peterson (1984). Whether this phenomena is a result of the newly developed technique being more effective in extracting the aromatic nitrogen components from the shale oils cannot be determined from the information currently available.

The extracted basic nitrogen fraction of the New Brunswick shale oils amount to 29 to 41% of that of the Colorado shale oil (Table 1). The Albert Mines sample exhibits the higher content of basic nitrogen extract.

TABLE 1. Nitrogen Analyses Results

Shale Oil Sample	elemental nitrogen content of the raw shale oils		basic nitrogen extract isolated from the raw shale oils			elemental nitrogen content of the basic nitrogen extracts		basic elemental nitrogen content of the raw shale oils	
	absolute	relative to Colorado	absolute		relative to Colorado	absolute	relative to Colorado	absolute	relative to Colorado
	(%)	(%)	(%)	average	(%)	(%)	(%)	(%)	(%)
Colorado:									
New Paroho	1.92	100.0	6.01 6.12	6.07	100	5.57	100	0.34	100
New Brunswick:									
Albert Mines	1.07	55.7	2.56 2.41	2.49	41	5.77	104	0.14	41
dolomite marlst	0.97	50.5	1.74 1.80	1.77	29	6.42	115	0.11	32

Analyses of the elemental nitrogen contained in the basic nitrogen extracts indicate (Table 1) that the basic nitrogen content of the extracts from the New Brunswick shale oil samples is in fact higher, between 104 and 115%, than that of the Colorado shale oil. As a result, the calculated basic nitrogen content of the raw New Brunswick shale oils amount to between 32 and 41% of that of the raw Colorado shale oil. In absolute terms, the Colorado shale oil contains 0.34% basic nitrogen, the Albert Mines shale oil, 0.14% and the dolomite marlstone shale oil, 0.11%.

The infrared spectra of the basic nitrogen fraction extracted from the Colorado shale oil (Appendix 2) differs considerably from that of the New Brunswick shale oils (Appendix 2) in the 1800 to 2800 cm^{-1} region. Two broad peaks appear in the Colorado shale oil basic nitrogen fraction, but do not exist in the New Brunswick (Albert Mines) spectra. This difference indicates the presence of different organic components in the shale oils from Colorado and New Brunswick. The difference in organic constituents may result from differences in processing conditions between the retorts used by New Paraho and Petrobras. Stronger absorptions in the 730 to 760 cm^{-1} and 1600 to 1635 cm^{-1} regions of the infrared spectra confirm the presence of abundant aromatic compounds in both the Colorado and New Brunswick extracts. This demonstrates the effectiveness of the RPC technique developed to yield the basic nitrogen extracts which contain the aromatic components of the raw shale oils.

Gas chromatographic analysis of the basic nitrogen extract (Appendix 3) of the Colorado sample indicates that it contains three high boiling point components (retention time 15.53, 16.72 and 18.08) in greater concentration than found in the New Brunswick (Albert Mines) sample; component concentration is directly proportional to the area under its respective curve. The significance of the increased quantities of these three components in the Colorado sample versus the New Brunswick sample could be due either to an inherent compositional difference in the kerogen content of the raw oil shales or to differences in the processing

conditions used to produce the shale oils. At this stage in the study no effort was made to identify the components represented by these chromatograph peaks. The significance of the gas chromatography in terms of asphalt durability is also, at this stage of the studies, uncertain.

4.0 CONCLUSIONS

1. The concentration of elemental nitrogen in raw New Brunswick shale oil is 50.5 to 55.7% (in dolomite marlstone zone and Albert Mines zone shale oils, respectively) of that in Colorado shale oil.

2. The concentration of basic nitrogen components in raw New Brunswick shale oil is 29 to 41% (in dolomite marlstone zone and Albert Mines zone shale oils, respectively) of that in Colorado shale oil.

3. The concentration of basic elemental nitrogen in the basic nitrogen extract of New Brunswick shale oil is 104 to 115% (in Albert Mines zone and dolomite marlstone zone shale oils, respectively) of that in Colorado shale oil.

4. The concentration of basic elemental nitrogen in the raw New Brunswick shale oils is 32 to 41% (in dolomite marlstone zone and Albert Mines zone shale oils, respectively) of that in Colorado shale oil.

5. It has been determined from previous studies that blended asphalt incorporating up to 20% Colorado shale oil asphalt with petroleum asphalt are preferred since pure shale oil asphalt are known to suffer from accelerated oxidative hardening. It is therefore conceivable that asphalt blends incorporating New Brunswick shale oil asphalt in concentrations up to double that of Colorado shale oil asphalt may exhibit qualities of enhanced durability and acceptable oxidative hardening. In addition, the production of nitrogen-bearing pavement recycling oil may be feasible.

6. The question of whether the properties of enhanced pavement durability observed in shale-oil-based asphalt are

directly proportional and solely attributable to their content of basic nitrogen components remains open. L. Lukens (personal communication, 1989) of the New Paraho Corporation, for example suggests that although basic nitrogen is a factor, it is not the only factor and therefore can not be used solely as a reliable means of quantifying pavement performance. Shale oil asphalt production, blending and performance testing is the only method of true evaluation of performance.

5.0 RECOMMENDATIONS

In order to unequivocally determine whether New Brunswick shale oils offer any potential as a source of asphalt having superior durability it will be necessary to produce samples of shale oil asphalt for testing purposes. These asphalt must be characterized and used in the preparation of samples of asphaltic concretes and tested in a manner similar to those procedures used in testing conventional asphaltic concretes. In addition, the feasibility of producing nitrogen-bearing pavement recycling agents from New Brunswick shale oil warrants evaluation.

Discussions concerning the production and testing of shale oil asphalt have been undertaken with Dr. M.R. Wilson of CANMET's Energy Research Laboratories in Ottawa. As a result of those discussions the following work proposal was prepared as a recommendation for further work.

New Brunswick shale oil would be distilled to produce an asphalt with a penetration value of 85-100 (ASTM Procedure D5) and blended with an appropriate conventional asphalt from Atlantic Canada to obtain blends of 5%, 10%, 25%, 40% and 50%. The properties of these blends together with pure shale oil asphalt and conventional asphalt would be investigated through the preparation of asphaltic concrete samples and their testing in a manner similar to which the Colorado oil shale asphalt have been tested.

Task 1 - Acquisition of Asphalt

a) shale oil: 5-10 gallons of sample to yield 1 gallon of asphaltic residue

b) conventional asphalt: 2 gallons of an appropriate conventional asphalt

c) aggregate: 5 gallons of an appropriate aggregate for preparation of briquets for freeze-thaw tests.

Task 2 - Distillation and Blending

The shale oil shall be distilled to produce 1 gallon of 85-100 penetration asphalt or other grade (either penetration or viscosity graded) if necessary. The initial distillation shall be at atmospheric pressures to about 200°C and then continued under reduced pressure to avoid excessive temperatures.

Five blends containing 5%, 10%, 25%, 40% and 50% of shale oil asphalt with the conventional asphalt sample shall be prepared in adequate amounts for subsequent tasks.

Task 3 - Routine Tests (AASHTO and/or ASTM)

The following tests shall be performed on the 5 blends, the shale oil asphalt and conventional asphalt samples:

Viscosities at 25°, 60° and 135°C
Penetrations at 25° and 4°C
Softening Points
Specific Gravity at 25°C
Ductility at 25°C
Solubility ($CHCl_3$: CCl_4)
Flash + Fire Points
Spot Test
Thin-Film Oven Test
- penetration of residue at 25°C
- ductility of residue at 25°C
- viscosity of residue at 60°C
- loss of material during test

Hardening Index - to be calculated using TFOT results (at least initially)

Penetration Index - to be calculated from penetration values at different temperatures

Elemental Analyses - carbon, hydrogen, nitrogen, sulphur and oxygen; vanadium, nickel, iron and other metals.

Task 4 - Non-Routine Tests

Freezing and Thawing Tests

Water susceptibility tests shall be made according to the method developed by the Western Research Institute in Laramie, Wyoming (Plancher, et al., 1982). Briquets shall be made of the six asphaltic samples that are mixed with aggregate for subjecting to freezing and thawing cycles. These briquets shall be prepared using a narrow particle size range of crushed and sieved aggregate with appropriate amounts of asphaltic materials (usually 5%). These briquets, after being fixed to pedestals, shall be subject to freezing and thawing cycles in water until cracks begin to appear. The number of cycles before cracking is a measure of resistance to stripping of asphalt from aggregate by water during freezing and thawing.

Asphaltene Settling Tests

These tests shall be carried out on the 7 asphaltic samples also according to a method developed by the Western Research Institute.

Note: The value of this test is controversial, but is claimed to give a measure of small changes in asphalt composition and an indication of the dispersibility of asphaltenes in n-hexane. The dispersion of asphaltenes in asphalt is considered important to asphalt compatibility and durability. This aspect is being studied as part of a contract by the Alberta Research Council for the Energy Research Laboratories. The outcome of this work should enable an informed decision to be made on whether or not to carry out this test.

Task 5 - Characterization

The shale oil asphalt and the conventional asphalt shall be separated into saturate, naphthene-aromatic, polar-aromatic and asphaltene fractions according to ASTM procedure 4124. In addition the asphaltenes of all blends shall be determined. Infrared spectra shall be obtained of all of these fractions and the significant peaks shall be interpreted in terms of functional groups and hydrocarbon structures. The range of basicity levels for the shale oil asphalt and the conventional asphalt should be determined by non-aqueous titration. (The basic nitrogen compounds are probably pyridinic but some of the more basic nitrogen groups such as aimes might also be present.) The pyrollic (non-basic) nitrogen groups shall be quantatively determined by infrared spectrometry.

6.0 REFERENCES

Filho, F.F., Vasconcelos, D. and Novicki, R.E.M. 1989. New Brunswick oil shale: technological characterization and Petrosix pilot plant retorting tests. New Brunswick Department of Natural Resources and Energy, Minerals and Energy Division, Open File Report OF89-45, 160 p.

Plancher, H. and Petersen, J.C. 1984. Nitrogen-containing components from shale oil as modifiers in paving applications. Symposium on Characterization and Chemistry of oil shales presented before the Divisions of Fuel Chemistry and Petroleum Chemistry, Inc., American Chemical Society, St. Louis, pp. 229-237.

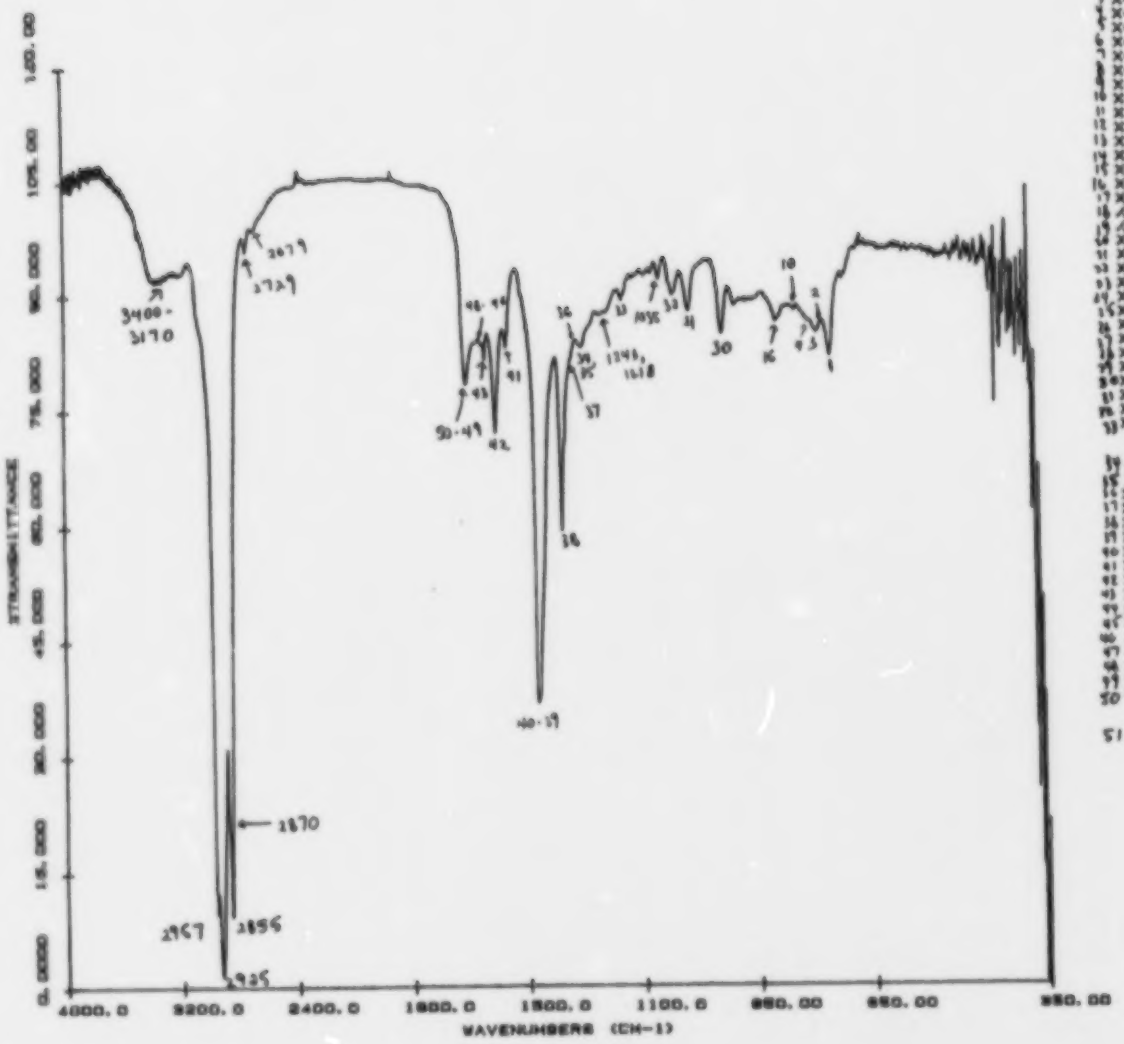
Plancher, H., Smith, E.B., Petersen, J.C. and Anagonos, J.N. 1982. Basic nitrogen compounds from shale oil and coal liquids as asphalt modifiers in paving applications; Proceedings of the Pan-Pacific Synfuels Conference '82, Tokyo, The Japan Petroleum Institute, Toshima-Ku, Tokyo, 11 p.

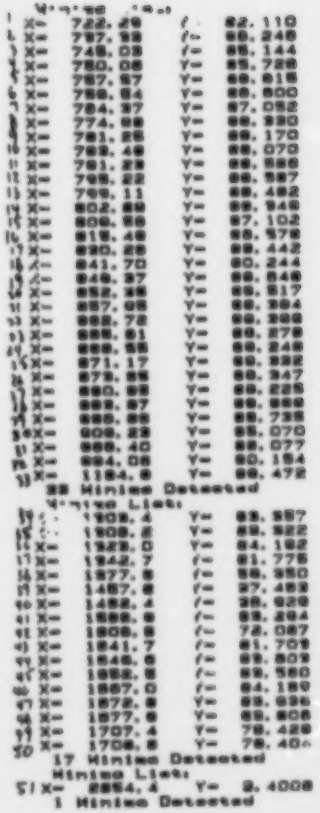
St. Peter, C. 1984. Mineralogical and chemical data of Albert Formation oil shale. New Brunswick Department of Natural Resources, Mineral Resources Division, Open File Report 84-4, 228 p.

Three-D GeoConsultants Ltd. 1989. Evaluation of New Brunswick shale oil for its potential as an asphalt feedstock. New Brunswick Department of Natural Resources and Energy, Minerals and Energy Division, Open File Report OF89-5, 81 p.

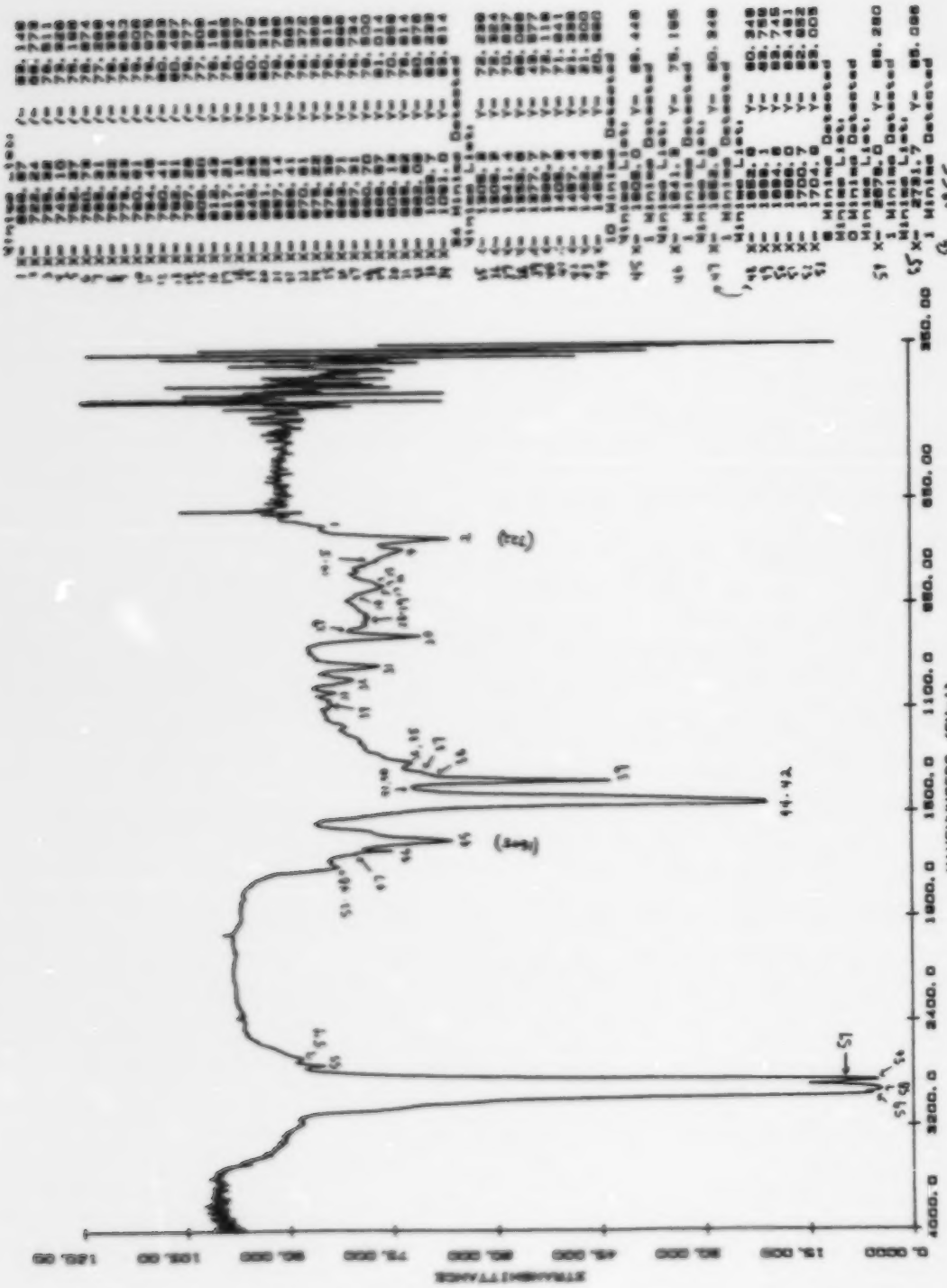
APPENDIX 1

INFRARED SPECTRUM OF THE RAW SHALE OILS

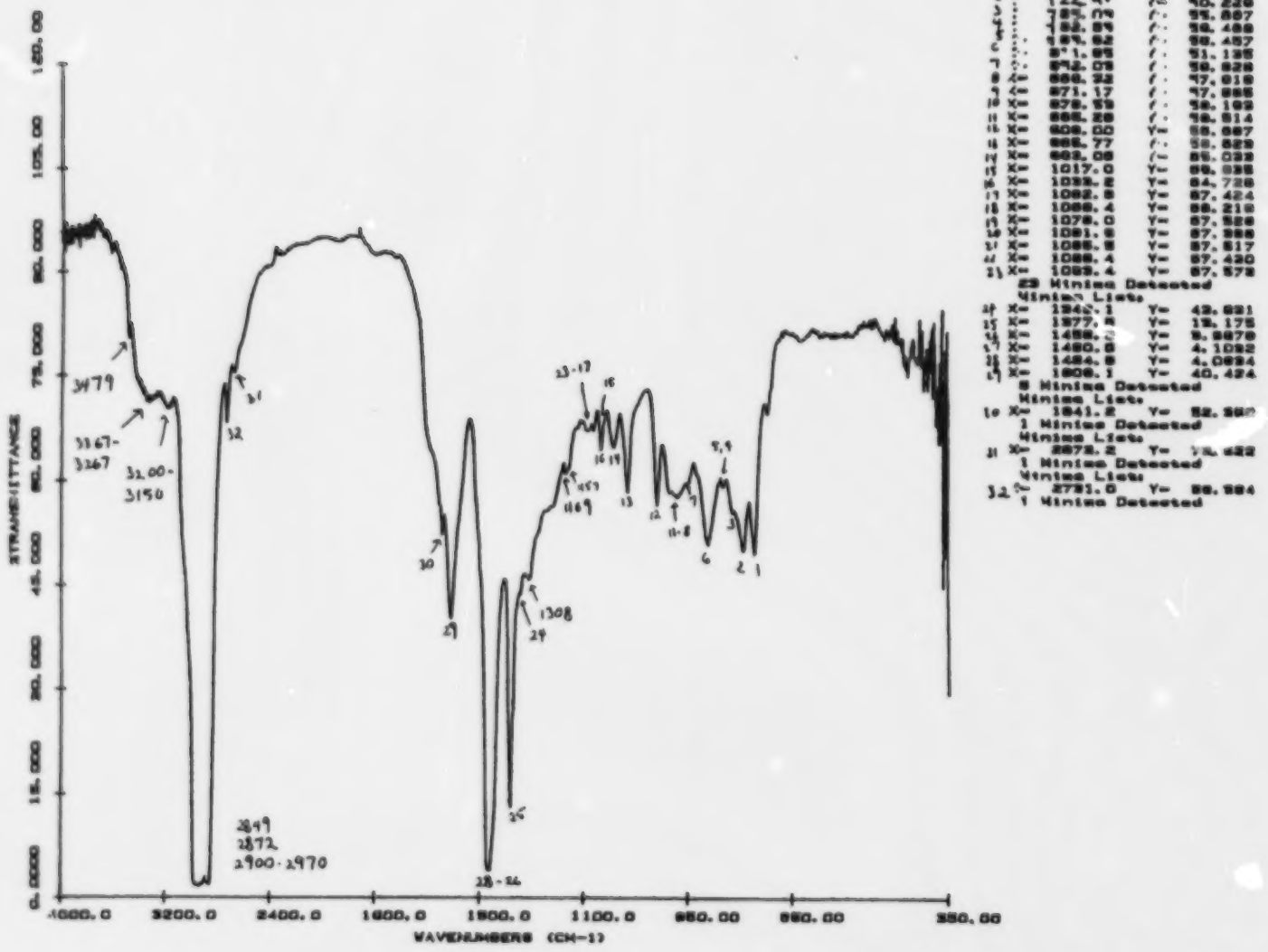




Appendix 1A. Infrared spectrum of the raw Colorado shale oil



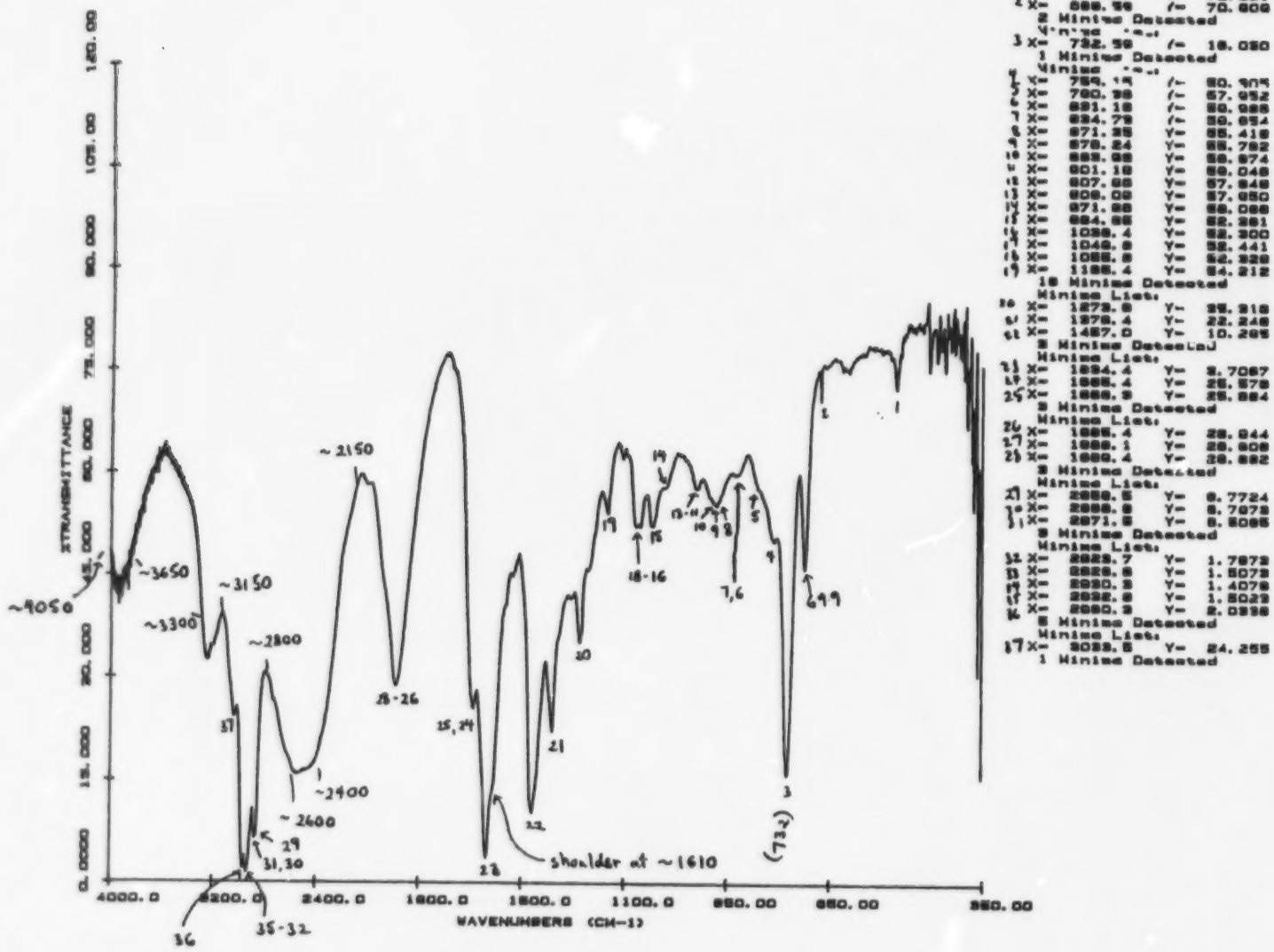
Appendix 1B. Infrared spectrum of the raw Albert Mines (New Brunswick) shale oil



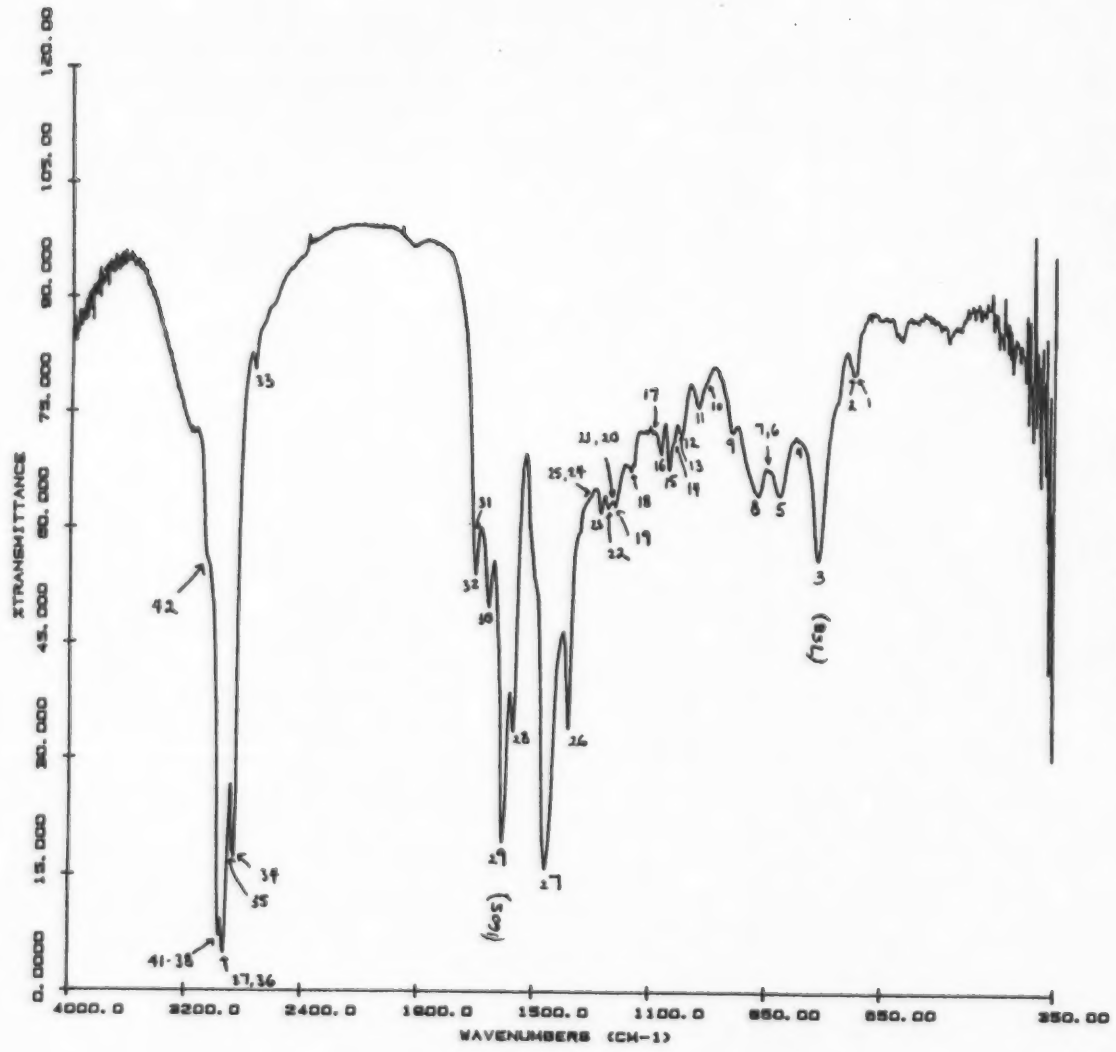
Appendix 1C. Infrared spectrum of the raw Dolomite Marlstone (New Brunswick) shale oil

APPENDIX 2

INFRARED SPECTRUM OF THE EXTRACTED BASIC NITROGEN FRACTIONS



Appendix 2A. Infrared spectrum of the basic nitrogen fraction extracted from the Colorado shale oil



Minima List:

1	X=	884.43	Y=	80.597
2	X=	888.08	Y=	80.518
3	X=	788.38	Y=	56.184
4	X=	792.40	Y=	71.719
5	X=	826.20	Y=	84.544
6	X=	842.45	Y=	87.588
7	X=	846.21	Y=	87.884
8	X=	883.42	Y=	84.497
9	X=	907.03	Y=	72.709
10	X=	982.49	Y=	78.447
11	X=	986.34	Y=	78.027
12	X=	985.28	Y=	72.487
13	X=	988.58	Y=	72.802
14	X=	1018.1	Y=	71.581
15	X=	1034.0	Y=	87.841
16	X=	1062.7	Y=	88.844
17	X=	1088.8	Y=	72.579

17 Minima Detected

Minima List:

18	X=	1185.8	Y=	87.580
19	X=	1220.4	Y=	83.014
20	X=	1230.0	Y=	83.704
21	X=	1241.7	Y=	83.092
22	X=	1245.2	Y=	82.833
23	X=	1288.2	Y=	82.144
24	X=	1287.8	Y=	85.284
25	X=	1290.0	Y=	85.258

8 Minima Detected

Minima List:

26	X=	1377.8	Y=	34.088
27	X=	1458.0	Y=	18.888
28	X=	1588.0	Y=	32.885
29	X=	1804.8	Y=	10.388
30	X=	1852.8	Y=	48.884
31	X=	1885.4	Y=	59.762
32	X=	1700.8	Y=	54.088

7 Minima Detected

Minima List:

33	X=	2791.4	Y=	80.838

1 Minima Detected

Minima List:

34	X=	2857.2	Y=	17.281
35	X=	2870.8	Y=	17.882
36	X=	2923.7	Y=	8.2880
37	X=	2927.4	Y=	4.8827
38	X=	2945.1	Y=	8.2080
39	X=	2954.8	Y=	7.3802
40	X=	2958.8	Y=	7.0835
41	X=	2958.8	Y=	7.2180

8 Minima Detected

Minima List:

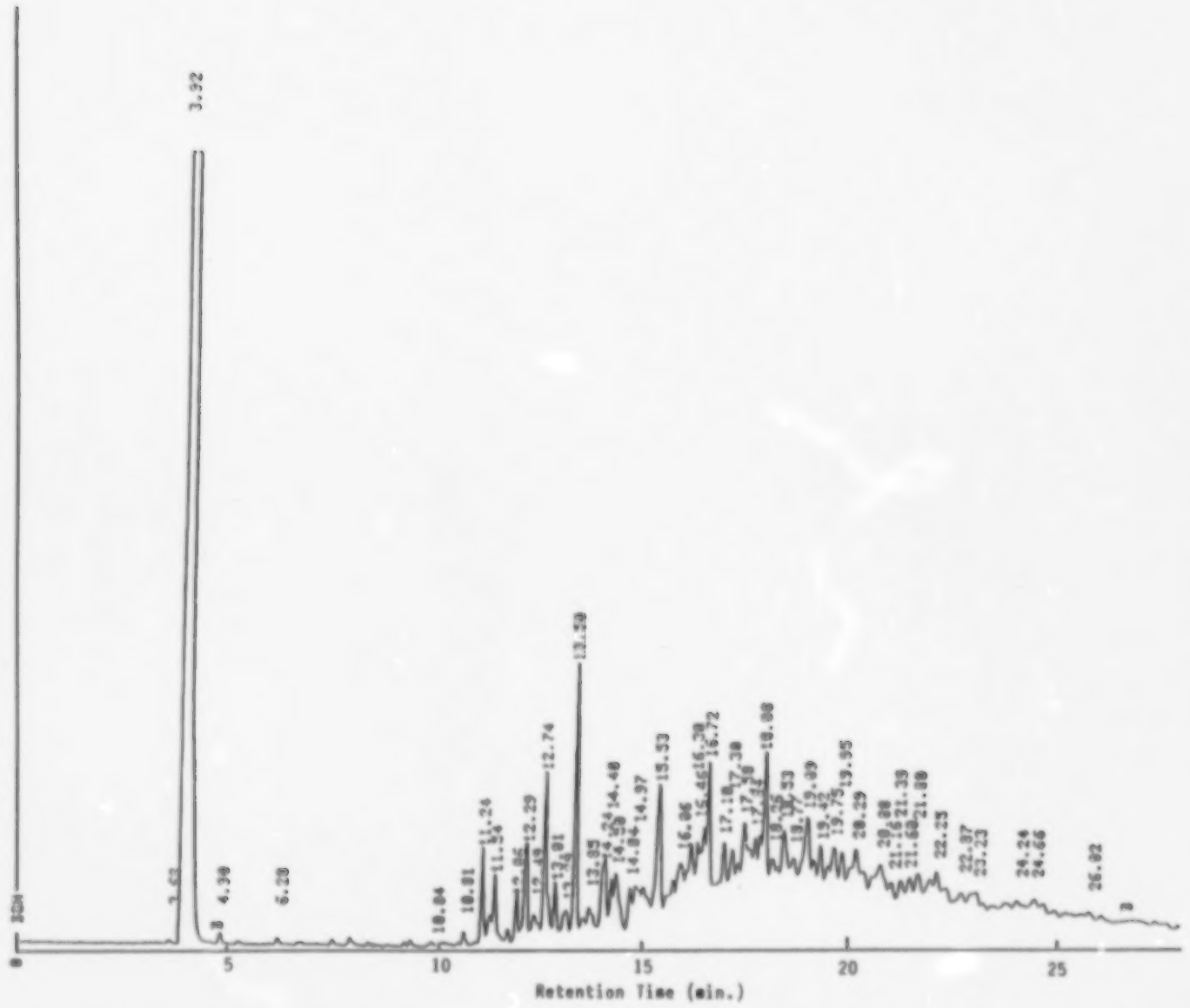
42	X=	3048.1	Y=	55.885

1 Minima Detected

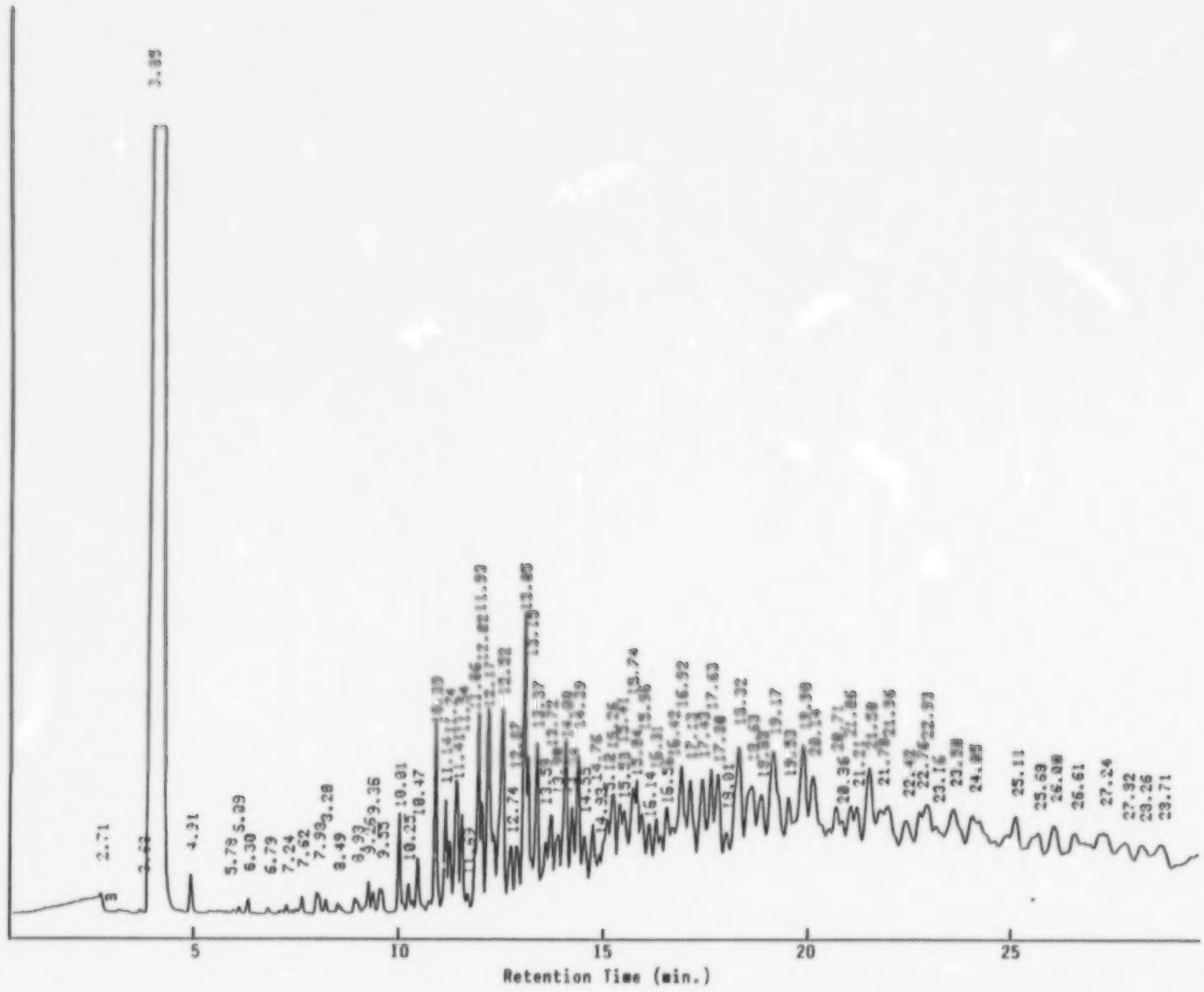
Appendix 2B. Infrared spectrum of the basic nitrogen fraction extracted from the Albert Mines (New Brunswick) shale oil

APPENDIX 3

GAS CHROMATOGRAPH TRACES OF THE EXTRACTED BASIC NITROGEN FRACTIONS



Appendix 3A. Gas chromotograph trace of the basic nitrogen fraction extracted from the Colorado shale oil



Appendix 3B. Gas chromotograph trace of the basic nitrogen fraction extracted from the Albert Mines (New Brunswick) shale oil